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含相邻五元环富勒烯（C_{50}、C_{56}、C_{60}）的氯稳定化及其氢化、氧化反应

Chlorinated stabilization, hydrogenation and oxidation upon fused-pentagon fullerenes (C_{50}, C_{56}, C_{60})

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Chlorinated stabilization, hydrogenation and oxidation upon fused-pentagon fullerenes (C_{50}, C_{56}, C_{60})

A Dissertation Submitted to the Graduate School in Partial Fulfillment of the Requirements for the Degree of Master Philosophy

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摘 要

自 1985 年 C_{60} 被发现以来，富勒烯的研究取得了长足的进步，尽管在此期间发现了很多富勒烯的新成员，独特的结构和物化性质也都表明其在生活和科研的各个方面都有着广泛的应用前景，然而目前真正得到商业化的仅有包括 C_{60} 在内有限的几种，这主要是因为大多数富勒烯结构中相邻五元环的存在，违背了 IPR(Isolated Pentagon Rule)规则，因而十分活泼，难以被捕获，此类富勒烯即非 IPR 富勒烯。富勒烯研究的重点之一即非 IPR 富勒烯的稳定化。理论研究表明许多富勒烯的非 IPR 异构体可能是稳定富勒烯形成的中间体，因而对于富勒烯形成机理的探索不可或缺。通过对这些活泼富勒烯的捕获，从实验上揭开这些神秘大分子的结构及性能。

目前非 IPR 富勒烯主要是通过石墨电弧放电法以内嵌或外接的方式得以稳定下来。本实验室于 2004 年成功捕获并表征了第一个外接衍生化的非 IPR 富勒烯 $C_{50}Cl_{10}$, 之后通过改进方法优化条件又相继得到了近 20 种含相邻五元环富勒烯。本论文的工作即对采用石墨电弧放电法引入氯源而得到的氯化富勒烯进行高效液相色谱分离，得到了两种新型非独立五元环富勒烯异构体 C_s-$^{\#1,809}C_{60}Cl_8$、C_2-$^{\#916}C_{56}Cl_{12}$，对其进行了确切的表征，并对 C_s-$^{\#1,809}C_{60}Cl_8$ 进行氢化反应研究。分离过程中还得到第一个小富勒烯氧化物 $C_{50}Cl_{10}O$，对其结构及氧化机理进行了探讨和实验验证。本论文主要内容共分为五个部分：

第一章：介绍了富勒烯的发现之旅、合成方法、及其在各个领域应用的研究现状。重点对富勒烯家族中化学性质活泼，难以捕获的非 IPR 富勒烯及其稳定方法—内嵌和外接衍生化进行了介绍，非 IPR 富勒烯本身具有的反应活性恰恰是富勒烯衍生化得到具有优良性能的新材料的前提，因此发现新的非 IPR 富勒烯及对其性能进行表征显得尤为重要，以此为主线，本论文的实验工作得以开展。

第二章：继本实验室成功表征 $C_{60}Cl_8$ 的两种异构体：I_h-$C_{60}Cl_8$，C_{2v}-$^{\#1809}C_{60}Cl_8$ 之后，其第三种异构体 C_s-$^{\#1809}C_{60}Cl_8$ 得以明确表征。此异构体具有与 C_{2v}-$^{\#1809}C_{60}Cl_8$ 相同的碳笼，但外接氯原子的方式发生了变化，与本实验室不久前表征的 C_s-$^{\#1809}C_{60}H_8$ 结构上却十分吻合，基于此，对这两种$^{\#1809}C_{60}Cl_8$ 进行了

氢化实验，反应产物分析发现了 C_s 及 C_{2v}-$^{\#1809}C_{60}H_8$ 两种异构体，本章重点对此进行了阐述和探讨。

第三章：本章将介绍 C_{56} 的第三个异构体 D_2-$^{\#916}C_{56}$ 以 C_2-$^{\#916}C_{56}$ Cl_{12} 的形式成功被捕获并得以表征。发现 C_{60} 的气相实验，同时也揭示了小富勒烯 C_{56} 仅次于 C_{60}、C_{70} 的可观强度，这使得其作为活泼的小富勒烯的代表被广泛研究。C_{56} 理论上有 924 种异构体，C_s-$^{\#864}C_{56}$，C_{2v}-$^{\#913}C_{56}$，C_2-$^{\#843}C_{56}$ 及 D_2-$^{\#916}C_{56}$ 是其中能量最低的四个异构体。C_s-$^{\#864}C_{56}$， C_{2v}-$^{\#913}C_{56}$，已于最近分别以 $^{\#913}C_{56}Cl_{10}$ 和 $^{\#864}C_{56}Cl_{12}$ 的形式捕获下来并得到确切表征。本章还对 C_2-$^{\#916}C_{56}Cl_{12}$ 的紫外可见光谱和循环伏安曲线进行了测定，结果显示了其良好的光电性能，预示着其在太阳能电池等光电领域中的潜在应用。

第四章：在对石墨电弧放电法合成得到的混合物的分离过程中得到 C_{50} 的第一个氧化物 $C_{50}Cl_{10}O$，X-单晶衍射表征确切无误地揭示了其环氧化结构。为了探究氧原子来源设计了一系列以 $C_{50}Cl_{10}$ 为反应物的对照实验，实验结果表明在氧气的存在下，$C_{50}Cl_{10}$ 可通过紫外辐射得到，其光谱表明其与分离得到的 $C_{50}Cl_{10}O$ 为同一化合物，从而证实了其光致氧化机理。本章将对其结构和氧化机理的实验验证过程进行阐述和分析。

第五章：本论文涉及工作的总结及后续的工作的展望。

关键词：非 IPR 富勒烯异构体 富勒烯衍生化 X-单晶衍射表征

Abstract

Since the discovery of fullerene C_{60} in 1985, studies on fullerenes have achieved progress on a wide range of research fields. In spite of many new members in this huge family being discovered and their potential in a variety of applications owing to their unique cagey structure and physicochemical properties, only C_{60} is used commercially in addition to a few of larger fullerenes such as C_{70}. Fused pentagons in fullerenes can be a reason for this situation. By violating Isolated Pentagon Rules (IPR), these fused-pentagon fullerenes (non-IPR fullerene) are very reactive and hard to be captured. Therefore, one of the main directions on fullerene research is the stabilization of non-IPR fullerenes, as many non-IPR isomers are supposed to be intermediates towards stable fullerenes theoretically, which is of importance to reveal the formation mechanism of fullerenes. Availability of these molecules also facilitates the functionalization fullerenes, leading to the discovery of novel fullerene-related materials.

Now there are mainly two approaches to stabilize non-IPR fullerenes: endohedral and exohedral derivatization. We successfully captured the first exohedral fullerene $C_{50}Cl_{10}$ by in-situ chlorination during the synthesis of fullerenes. By modifying and optimizing the synthesis conditions, nearly 20 non-IPR fullerenes have now been captured and characterized by X-ray diffraction. In this dissertation, separation and characterization of novel non-IPR fullerene species, C_s-$^{\#1809}C_{60}Cl_8$, C_2-$^{\#916}C_{56}$ Cl_{12} as well as the first smaller fullerene oxide $C_{50}Cl_{10}O$ are reported. To investigate the reactivity of non-IPR fullerenes, hydrogenation upon C_s-$^{\#1809}C_{60}Cl_8$ and oxidation involving $C_{50}Cl_{10}$ were carried out and the mechanism were discussed in detail. Five parts are included as follows:

Chapter 1: Introduction of history, synthesis and applications of fullerenes, among which the two approaches for stabilizing labile non-IPR fullerenes are represented. Given that the reactivity of non-IPR fullerenes can result in enrichment

of fullerene-involving functionalizations, some general reactions upon fullerenes are covered in this chapter.

Chapter 2: A novel isomer of $^{\#1809}C_{60}Cl_8$ has been characterized with ambiguous X-ray diffraction, revealing it the same non-IPR carbon cage as presently characterized C_{2v}-$^{\#1809}C_{60}Cl_8$ but with different chlorides addition pattern. This new isomer has a C_s symmetry which is quite alike of newly discovered C_s-$^{\#1809}C_{60}H_8$ structurally. For better comparison, hydrogenation upon the two $^{\#1809}C_{60}Cl_8$ isomers was carried out. It was shown that both the two $^{\#1809}C_{60}Cl_8$ isomers could give birth to C_s and C_{2v}-$^{\#1809}C_{60}H_8$ respectively.

Chapter 3: A new C_{56} carbon cage of D_2-$^{\#916}C_{56}$ has been stabilized in the form of C_2-$^{\#916}C_{56}Cl_{12}$. The gas phase experiment revealed the enhanced intensity of smaller fullerene C_{56}, which has the second prevalence to C_{60} and C_{70}. So C_{56} is the representative member in the family of labile smaller fullerenes. Among all the 924 isomers, C_s-$^{\#864}C_{56}$, C_{2v}-$^{\#913}C_{56}$, C_2-$^{\#843}C_{56}$ and D_2-$^{\#916}C_{56}$ are the four with lowest energy, C_s-$^{\#864}C_{56}$ and C_{2v}-$^{\#913}C_{56}$ have been characterized in the form of $^{\#913}C_{56}Cl_{10}$ and $^{\#864}C_{56}Cl_{12}$. In this part, UV/Vis spectrum and cyclic voltammogram(CV) measurements were performed upon this new isomer to reveal its absorption and electrochemical properties, showing the new isomer potential in photovoltaic application.

Chapter 4: In the isolation for the mixture from arc-discharge of graphite, the first oxide of C_{50} was obtained. By X-ray diffraction, its epoxide structure has been characterized ambiguously. In order to search for the oxygen source, a series of control experiments, with $C_{50}Cl_{10}$ as reactant, were designed and carried out. Interestingly, $C_{50}Cl_{10}$ with UV irradiation and oxygen coexisting can generate the same $C_{50}Cl_{10}O$ as obtained for the arc-discharge.

Chapter 5: Conclusions to all the works related to this dissertation are summarized, and the future studies are prospected.

Key words: non-IPR fullerene; hydrogenation; oxidation